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CONTRACTOR NAME:

CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129

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PRINCIPAL INVESTIGATORS: F. P. Burke, S. D. Brandes, and R. A. Winschel

SUBCONTRACTORS/PRINCIPAL INVESTIGATORS:

- University of Kentucky Center for Applied Energy Research - F. J. Derbyshire, G. Kimber, R. K. Anderson, S. D. Carter
- LDP Associates - M. Peluso

CONTRACTING OFFICER'S REPRESENTATIVE: M. A. Nowak

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SUMMARY OF TECHNICAL PROGRESS - OVERALL

Activities this quarter were conducted under Tasks 2, 3, and 5. Task 2 work concentrated on evaluating the effects of low-severity, first-stage reaction conditions on coal conversions of lignite, subbituminous, and bituminous coals. The impact of artificially weathering bituminous coal was investigated. Large quantities of first-stage product were made using the one-liter reactor for subsequent filtration and catalytic upgrading tests. Test conditions and coal conversions for all microautoclave and one-liter tests made this quarter are presented in Table 1. Filtration tests examined lignite, subbituminous, and bituminous coal products. The effects on resid conversion of second-stage reaction conditions and

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catalyst recycle were studied. Task 3 work included the successful transfer of first-stage reactor products to a receiver and the design of an interstage filter. Task 5 work included an ongoing review of the technical and patent literature and expansion of the annotated bibliography. Mass and elemental balances were obtained for selected tests.

Key accomplishments are the following:

- High coal conversions (up to 93.4%) were obtained with Ohio 11 Mine Kentucky bituminous coal at low-severity conditions.
- Mass and elemental balance data for microautoclave tests continue to show an enrichment of the first-stage product with hydrogen and oxygen depletion compared to the starting coals.
- A successful transfer of first-stage reaction products to a receiver vessel was accomplished. The transfer, as executed, provides the preliminary information necessary to proceed with the insertion of a filter between the reactor and the receiver vessel.
- Elevation of total reaction pressure with steam improves coal conversion of Glenharold Mine lignite, whereas increasing reaction pressure with nitrogen does not.
- Large samples of first-stage product were produced using the one-liter reaction system; samples up to 450 g can be made in a single test for use in filtration and second-stage reaction testing.
- Analyses of solvent recovered from one-liter autoclave tests show the materials to be essentially unchanged from the material fed to the reactor. This information indicates that solvent recycle is potentially viable.

- Filtration of subbituminous coal and lignite first-stage products is rapid; filtration of bituminous coal first-stage product is dependent on the first-stage solubilization temperature.
- Catalytic upgrading of first-stage products results in higher resid conversions than that obtained with a conventional two-stage liquefaction-produced deashed resid at the same conditions.
- Preliminary data indicate that catalyst activity is maintained on recycle in the second-stage reaction.
- Single-pass resid conversion of filtered, first-stage resid product of high ash, high-sodium-content Freedom Mine lignite at 440 °C, with 1 wt % Mo catalyst was ~75 wt %.

SUMMARY OF TECHNICAL PROGRESS - BY TASK

Task 2 - Evaluation of Process Steps

Microautoclave Tests

Tests were made with Ohio 11 Mine bituminous coal at various conditions. Coal conversion obtained for a thermal case at 350 °C, 60 min, was 45 wt %. With hydride ion reagent "A" present at 350 °C, 60 min coal conversion averaged 90 wt %. A series of microautoclave tests were made for filtration tests with Ohio 11 Mine coal at different temperatures between 300 and 400 °C (see below).

Two microautoclave tests were made with a sample of Black Thunder Mine coal, which was artificially weathered (100 °C for 14 days in air). Test conditions were 350 °C, 60 min, Wilsonville Run 262E V1074 solvent, and hydride ion reagent "A". Reactor loadings were 17.5 g and 22.5 g; coal conversions were 61.0 and 66.2 wt %, respectively. These conversions are ca. 12 wt % (absolute) lower than coal conversions obtained with as-received Black Thunder coal in tests made under the same conditions. No further work with weathered coal is planned.

Mass and elemental balances of microautoclave tests were made with Ohio 11 Mine bituminous coal (Run 117) and Glenharold Mine lignite (Run 127b). Test conditions used for both runs were 60 min, 350 °C, Wilsonville Run 262E V1074 solvent, and hydride ion reagent "A". Water was added to the Glenharold Mine lignite reaction system. Good recoveries were obtained (95.5% for the Ohio 11 Mine bituminous coal test and 98.6% for the Glenharold Mine lignite test). The H/C molar ratio for the soluble 488 °C* product for both tests was higher than for the starting coal (0.84 vs. 0.82 for the Ohio 11 Mine coal and 1.06 vs. 0.84 for the Glenharold Mine lignite). Data from these tests were sent to LDP Assoc. for analyses (see below).

Glenharold Mine lignite conversion was improved by the addition of water to the reaction system. Coal conversion determined last quarter for reaction at 350 °C, 45 min, hydride ion (HI) reagent "A" to dry coal ratio of 1.1 was ca 70 wt %. In Run 127 and Run 127b, water was added to the reaction system; test conditions were 350 °C, 60 min, HI "A"/dry coal = 1.0. Coal conversions were 89.9 and 90.4 wt %, respectively. Elevation of the total

reaction pressure with nitrogen (Runs 120, 120B, 124) did not improve coal conversions. Total reaction pressure and steam pressure will be investigated next quarter.

To help determine the feasibility of solvent recycle, two distillate samples recovered from one-liter autoclave tests were analyzed. The 120 °C x 488 °C distillates from one-liter autoclave Runs 4-LA and 5-LA have the same boiling point range as the solvent fed. Gas chromatography/mass spectrometry analyses of the samples show little difference from that of the starting Wilsonville Run 262E V1074 488 °C solvent. These distillates will be retained for use in future microautoclave tests to confirm their serviceability in recycle.

One-Liter Autoclave

Five one-liter autoclave runs (Runs 4-LA, 4B-LA, 5-LA, 6-LA, and 7-LA) were successfully completed. The 115 °C⁺ product distillation cut from these four runs was sent to UK/CAER for filtration and catalytic upgrading tests. Runs 4-LA, 4B-LA, and 5-LA used Black Thunder Mine subbituminous coal, Run 6-LA was made with Ohio 11 Mine bituminous coal, and Run 7-LA used high ash and sodium-content Freedom Mine lignite. Run 7-LA was the first test of sample transfer (see Task 3, below). All tests used Wilsonville Run 262E V1074 solvent and hydride ion reagent "A". Approximately 450 g of feed can be processed per test. Mass balances were completed for Runs 4B-LA and 5-LA. About 95% of the feed is accounted for in each test. Coal conversions for one-liter autoclave runs 4-LA, 4B-LA, 5-LA, 6-LA, and 7-LA were calculated from THF-solubilities of grab samples. Coal conversions are within 3 wt% (absolute) of corresponding microautoclave test results for all tests except Run 4B-LA, which was 5 wt % less than the corresponding microautoclave test.

Filtration Studies

A filtration rig with an electrically-heated 200-mL capacity stainless steel filter and a 47-mm diameter screen was assembled and tested.

Samples from one-liter autoclave tests (Runs 4-LA and 5-LA) were filtered at 150 °C. Samples of ca. 80 g were warmed, with stirring, to 150 °C and then transferred to the filter. Filtration rates were rapid. However, some of the coal extract was not in solution at

150 °C. This was confirmed by analysis of the filter cake which had a low solids content; THF-insolubles were about 30%. The remainder of Run 5-LA material was filtered at 280 °C without problem. Filtration was very rapid (70 g in less than 1 minute); the filter cake had a 'normal' solids content (ca. 50% THF-insolubles). Both filtrates from Run 5-LA were vacuum distilled to give products for use in second-stage catalytic upgrading tests with about 70% 566 °C* (1050 °F*) material. Filtration at 280 °C gave a total 566 °C* filtrate fraction, which was substantially higher than that obtained at 150 °C. This provides further confirmation of the incomplete re-dissolution of the first-stage product at 150 °C.

Products of a second test made under the same conditions as Run 4-LA (Run 4B-LA) filtered rapidly in the 200-mL stainless steel filter at 275 °C and 14 psi. The 50 g filtrate was concentrated to give about 80% of the sample boiling above 566 °C for use in catalytic upgrading tests.

The products of first-stage reaction at 350 °C, 60 min, with Ohio 11 Mine bituminous coal (Run 6-LA) was difficult to filter. The first attempt in the 200-mL rig yielded only 3 g of filtrate from 60 g of feed after 10 minutes at 280 °C and 30 psi. The filter element used was the normal glass fiber supported on a 1-mm perforated plate. A micro-filter-rig run was performed on the same material using Conidur (100 µm orifices). The filtration rate was slow. The problem was filter cake properties, not blocking of the media. This character is to be expected of bituminous coals after mild digestion. First-stage microautoclave tests made at 300 °C (Runs 123a and 123b) and 400 °C (Runs 121a and 121b) with the bituminous coal were prepared by CONSOL and examined at the CAER. The 400 °C material filtered quickly (10 minutes at 270 °C) and gave a filter cake with 50% ash in the THF-insolubles, indicating a 94% conversion. The 300 °C material appears to be a dry powder. This is indicative of the coal swelling at low solvent:coal ratio such that all particles are touching another. No attempt was made to filter this sample. Samples made by CONSOL at 370, 380, and 390 °C (Runs 128, 129, and 130) will be examined next quarter.

The 115 °C* distillation fraction of the product from a one-liter autoclave test (Run 7-LA) which was made with high ash and sodium-content Freedom Mine lignite, 350 °C, 60 min,

Wilsonville Run 262E V1074 solvent, and hydride ion reagent "A" was filtered. The sample was heated to 250 °C in a stirred stainless-steel vessel in order to re-solubilize the extract. The sample (ca. 200 g) then was transferred to the 200 mL filter rig and the rate of filtration through a glass fiber paper was monitored. With an over pressure of 15 psig, the filtration took ca. 20 minutes. A flat filter cake of 15 mm thickness formed. The filter cake was blown with nitrogen for 6 minutes at 10 psi, which resulted in a cake of around 70% insolubles. The cake was initially 50% insolubles which indicates that over half of the liquids in the wet filter cake can be removed by nitrogen blowing. The filtrate was vacuum distilled to give a concentrated feed for subsequent hydrocracking reactivity tests.

Second Stage Catalytic Upgrading

Microautoclave Experiments

Low-temperature (400 °C and 420 °C) catalytic upgrading experiments were performed in microautoclaves using 3 g of Wilsonville Run 258A deashed residuum (DAR) and 1000 ppm of Mo added as Molyvan L. Comparison was made to runs at 440 °C. At 420 °C, gas production and residuum conversion were intermediate to the results obtained at 400 °C and 440 °C. These results indicated that operation at 420 °C may be a favorable compromise to potentially high gas generation obtained at 440 °C while maintaining high residuum conversion.

The catalyst recycle study continued using two experimental techniques. In the first, DAR was reacted for 60 minutes at 440 °C with 1000 ppm Mo as catalyst. The non-gaseous products were collected and distilled to recover the residual fraction. After quenching, fresh DAR was added to bring the mixture to its original residuum content. The reactor was recharged with gas and the reaction was repeated under the same conditions. The results showed that residuum conversion diminished as additional reaction cycles were performed. It could not be determined from this information whether the activity of the catalyst was declining or the residuum was becoming more refractory. ¹H-NMR analyses were obtained for the 1050 °F⁺ resids of the hydrotreated Wilsonville DAR products and the feed DAR. Both product resids are more aromatic than the feedstock; this implies that they are less hydrogenated.

In the second test, the catalyst experienced two reaction cycles, while the DAR at the start of the second cycle was mostly fresh material. Molyvan L, sufficient to give 1000 ppm overall, was added to only 10% of the DAR, and this mixture was reacted at 440 °C for 60 min to simulate the first pass. The gases were collected, the reactor opened and the remaining 90% of the DAR was added and the second pass effected. This gave a second-pass residuum conversion of 34%, which compares favorably to the single-pass residuum conversion of 32% determined earlier using all fresh feedstock. It was concluded that the catalyst was retaining its activity upon recycle. The results from the first recycle test probably were due to the declining reactivity of the unconverted DAR.

Catalytic upgrading runs were made using composited, filtered, first-stage microautoclave products from Black Thunder Mine subbituminous coal tests (Runs 21, 26, 52, and 53) made last quarter. A 2 x 2 matrix of reactor temperature and Mo concentration (400/440 °C and 1000/ 10,000 ppm Mo) was completed with this material. In addition, catalytic upgrading runs were made with individual first-stage, filtered samples produced with lignite and bituminous coal. Compared to experiments utilizing Wilsonville Run 258A deashed residuum, the CONSOL filtrates are more readily converted to 1050 °F products. The reactivity of the distilled filtrate of a first-stage product made with Ohio 11 Mine Kentucky bituminous coal was evaluated. Conditions used for upgrading were 440 °C, 60 min, 1% Mo. Single pass resid conversion was ca. 55 wt %. The reactivity of the distilled, filtered, first-stage product made with Freedom Mine lignite (Run 7-LA) also was tested. Two tests were made, one at 400 °C, 60 min, 1% Mo and the second at 440 °C, 60 min, 1% Mo. Single pass resid conversion was ca. 50 wt % at 400 °C and 75 wt % at 440 °C.

Simulated Distillation Analysis

The high-temperature simulated distillation apparatus is now used to routinely determine the boiling point distribution of the vacuum distillation fractions of the products from catalytic upgrading experiments. An autosampler was added to the instrument; this has improved precision of the results. Simulated distillation has been useful for verifying the cut point temperature obtained by vacuum distillation. An inconsistency in the heating method for vacuum distillation was discovered which resulted in cut points lower than the

target value of 566 °C (1050 °F); conversions were corrected using the simulated distillation boiling point curves.

Task 3 - Flow Sheet Development

One-Liter Autoclave

A one-liter autoclave test was completed successfully using the Method 2 recovery procedure. In this procedure, the hot contents of the autoclave are transferred at the conclusion of the run to the receiver vessel located directly under the autoclave. The entire system was cooled, and gases were collected as in previous tests. This test (Run 7-LA) used Freedom Mine "high ash, high-sodium-content" lignite. After the run, the autoclave was opened; the walls of the autoclave had only a film of material left on them.

The transfer, as executed, provides the preliminary information necessary to proceed with the insertion of a filter between the reactor and the receiver vessel.

Filtration Studies

A preliminary design for a filter to be located immediately following the first-stage one-liter autoclave was completed.

Task 5 - Engineering and Economic Study

LDP Associates continued the review of the technical and patent literature on hydride transfer agents. Additions to the annotated bibliography were completed and the second update was issued. Several key articles were identified.

In an effort to elucidate the chemical mechanisms of the proposed process, material balances and elemental analyses of four microautoclave tests were evaluated. The microautoclave tests evaluated were made with Black Thunder Mine coal (Runs 73, 74b, and 76) and Ohio 11 Mine coal (Run 117). A procedure was developed to generate an elementally balanced material balance for these runs. This material balancing procedure adjusts the yields of the measured carbon-containing output streams to force ash and carbon balances. Yields of water, hydrogen sulfide, ammonia and gaseous hydrogen are then calculated to close the oxygen, sulfur, nitrogen and hydrogen elemental balances.

The results of these balances begin to indicate the effect of processing conditions and coal type on yield structure.

Task 6 - Reporting

Bi-monthly conference calls were held as scheduled with UK/CAER and LDP. Reports documenting the calls were issued. A meeting was held with LDP Associates at CONSOL R&D in Library, PA, on June 5, 1996, to discuss progress of the engineering and economic evaluation and plans for the direction of the project. A paper entitled "Exploratory Research for Novel Coal Liquefaction Concept" was submitted for the U.S. DOE First Joint Power and Fuel Systems Contractors Conference; a presentation for that meeting is in preparation.

TABLE 1

TASK 2 MICROAUTOCLAVE TEST DATA
FOR PERIOD 4/1/96 TO 6/30/96

Coal	Microautoclave Run/Date	Time (MIN)	Temp (°C)	Coal		Hydride Ion Reagent "A", g	Solvent g	Water g	HI "A" Dry Coal g:g	Solvent: Dry Coal g:g	Coal Conv. Wt % MAF Coal Basis	Comments
				g	Moisture, wt%	Ash, wt%						
Black Thunder Mine, Subbituminous	Run # 102b 04/01/96	60	350	5.37	21.1	5.54	6.25	10.00	0.88	1.5	2.4	81.4
	Run # 103 04/01/96	60	350	5.37	21.7	5.54	4.20	12.05	0.88	1.0	2.9	74.8
	Run # 106 04/03/96	60	350	5.37	22.1	5.54	6.25	15.00	0.88	1.5	3.6	81.8
	Run # 108 04/04/96	60	350	9.50	21.9	5.54	7.40	18.40	-	1.0	2.5	75.8
	Run # 109 04/15/96	60	350	5.37	21.8	5.54	4.18	15.00	-	1.0	3.6	75.2
	Run # 110 04/16/96	60	350	4.17	21.8	5.54	4.86	7.77	0.88	1.5	2.4	77.4
Weathered Black Thunder Mine, Subbituminous	Run # 118B 05/03/96	60	350	3.60	0.9	5.54	5.35	8.55	-	1.5	2.4	61.0
	Run # 119 05/06/96	60	350	4.48	0.9	5.54	6.88	11.00	-	1.5	2.5	66.1
Glenharold Mine lignite	Run # 120 05/07/96	60	350	4.50	11.6	9.48	4.38	8.76	-	1.1	2.2	71.9 950psig N2 added
	Run # 124 05/13/96	60	350	4.50	11.6	9.48	4.38	8.76	-	1.1	2.2	73.4 1100psi N2 added
	Run # 120B 05/14/96	60	350	4.50	11.6	9.48	4.38	8.76	-	1.1	2.2	73.0 950 psi N2 added
	Run # 127 06/06/96	60	350	5.15	11.6	9.48	4.59	11.01	1.75	1.0	2.4	89.9
	Run # 127B 06/26/96	60	350	5.15	11.0	9.48	4.59	11.01	1.75	1.0	2.4	90.4
Ohio 11 Mine, Bituminous	Run # 104 04/03/96	60	350	5.0	2.8	6.71	4.75	7.25	-	1.0	1.5	88.8
	Run # 105 04/03/96	60	350	4.39	2.8	6.71	4.19	12.06	1.86	1.0	2.8	91.1
	Run # 107 04/04/96	60	350	6.0	2.8	6.71	2.90	8.10	1.86	0.5	1.4	69.8
	Run # 111 04/09/96	60	350	5.00	2.8	6.71	4.85	7.15	-	1.0	1.5	90.1
	Run # 112 04/10/96	60	375	5.00	2.8	6.71	4.85	7.15	-	1.0	1.5	93.3
	Run # 113 04/10/96	30	350	5.00	2.8	6.71	4.85	7.15	-	1.0	1.5	78.8
	Run # 114 04/11/96	60	375	6.00	2.8	6.71	2.90	8.10	-	0.5	1.4	88.9
	Run # 115 04/11/96	60	350	4.39	2.8	6.71	6.28	9.96	1.86	1.5	2.3	63.2
	Run # 116 04/12/96	60	400	5.00	2.8	6.71	4.85	7.15	-	1.0	1.5	93.4
	Run # 117 04/15/96	60	350	5.00	2.8	6.71	4.85	7.15	-	1.0	1.5	86.7
	Run # 121A&B 05/08/96	60	400	5.00	2.8	6.71	4.85	7.15	-	1.0	1.5	NA Sample for filtration
	Run # 122B 05/08/96	60	300	5.00	2.8	6.71	4.85	7.15	-	1.0	1.5	NA Sample for filtration
	Run # 123A&B 05/17/96	60	300	5.00	2.8	6.71	4.85	7.15	-	1.0	1.5	NA Sample for filtration
	Run # 125B 05/17/96	60	350	5.00	2.8	6.88	-	8.00	-	0.0	1.6	44.9
	Run # 126 05/18/96	60	400	5.00	2.8	6.88	-	8.00	-	0.0	1.6	72.3
	Run # 128 06/24/96	60	370	5.00	2.8	6.88	4.85	7.15	-	1.0	1.5	NA Sample for filtration
	Run # 129 06/25/96	60	380	5.00	2.8	6.88	4.85	7.15	-	1.0	1.5	NA Sample for filtration
	Run # 130 06/26/96	60	390	5.00	2.8	6.88	4.85	7.15	-	1.0	1.5	NA Sample for filtration

TABLE 1 (Continued)

TASK 2 ONE-LITER AUTOCLAVE TEST DATA
FOR PERIOD 4/1/98 TO 6/30/98

Coal	One Liter Autoclave Run No.	Time (MIN)	Temp (°C)	Coal			Hydride Ion Reagent "A", g	Solvent g	Water g	HI "A" Dry Coal g:g	Solvent: Dry Coal g:g	Coal Conv. Wt % MAF Coal Basis (a)	Comments
				g	Moisture, wt%	Ash, wt%							
Black Thunder Mine, Subbituminous	4-LA	45	400	100.0	22.0	5.54	81	121	-	1.0	1.6	84.1	
	4B-LA	45	400	100.0	22.0	5.54	80	122	-	1.0	1.6	83.5	
	5-LA	150	350	100.0	22.0	5.54	80	100	-	1.0	1.3	84.4	
Ohio 11 Mine, Bituminous	6-LA	60	350	98.0	2.8	6.71	97	143	-	1.0	1.5	85.0	
Freedom Mine lignite (high ash & sodium content)	7-LA	60	350	94.0	11.8	11.42	125	202	31	1.5	2.4	86.3	hot transfer to receiver

a. determined from grab sample